

Self-Healing Nano-Textured Vascular-Like Materials: Mode I Crack

Propagation

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ABSTRACT

Here we investigate crack propagation initiated from an initial notch in a self-healing material. The crack propagation in the core-shell nanofiber mats formed by co-electrospinning and the composites reinforced by them is in focus. All samples are observed from the crack initiation until complete failure. Due to the short-time experiments done on purpose, the resin and cure released from the cores of the core-shell nanofibers could not achieve a complete curing and stop crack growth, especially given the fact that no heating was used. The aim is to elucidate

their effect on the rate of crack propagation. The crack propagation speed in PAN-Resin-Cure (PRC) nanofiber mats (with polyacrylonitrile, PAN, being the polymer in the shell) was remarkably lower than that in the corresponding monolithic PAN nanofiber mat, down to 10%. The nanofiber mats were also encased in polydimethylsiloxane (PDMS) matrix to form composites composite. The crack shape and propagation in the composite samples was studied experimentally and analyzed theoretically, and the theoretical results revealed agreement with the experimental data.

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1. Introduction

A fascinating natural phenomenon of complete or partial self-recovering from an injury always attracted attention from the engineering perspective. Self-healing materials have been designed to withstand failure of at a certain level of damage, for example, due to bending,¹⁻² stretching,³⁻⁵ delamination,⁶⁻⁷ etc. The healing agents were stored in capsules,⁸⁻¹¹ tubes^{2, 12-14} or nanofibers.^{7, 15-18} The healing agents are supposed to be released in the ruptured area, be cured and polymerize. They should bond the crack banks and prevent catastrophic failure. Nanofibers mimic the vascular system under our skin and hold great promise for development of self-healing composites. Such promising healing agent as liquid epoxy can be encapsulated inside nanofiber cores by co-electrospinning¹⁷⁻²⁰ or solution blowing.⁷ Such nanofibers form entangled nanofiber mats.

Composites are widely used in industry, e.g. in cars and aircraft, buildings, power plants, etc. Even though the mechanical properties of composites had been advanced for decades, delamination of the ply layers still poses a significant problem. It is extremely uncontrollable since even a tiny flaw can evolve into a catastrophic crack. Moreover, a small defect is neither easy to detect, nor to fix since it is located in the material bulk. That is the reason that it is highly risky to keep machines with composite parts operating for a long time under fatigue-prone conditions. Self-healing nanofibers embedded between the ply layers in composite can release healing agents when damaged by a propagating crack and prevent its further growth. Even though one cannot expect to completely prevent failure in the framework of this approach, at least crack propagation can be retarded. An additional benefit of self-healing nanofibers is in the fact that the entire healing process proceeds autonomously without any need for UV radiation, pH control or thermal assistance.

Most of the studies on self-healing materials aimed at a higher healing efficiency. A numbers of results revealed significant self-healing effects. However, severe problems can arise when a crack has already emerged and is developing. The question is what self-healing materials can contribute in such cases? Here we aim to elucidate this issue studying propagation of a pre-notched flaw in a strip under tension. Namely, nanofiber mats which revealed significant self-healing features³ are used in crack propagation experiments under mode I fracture conditions.

2. Experimental

2.1 Materials

Polymer polyacrylonitrile (PAN, $M_w = 150$ kDa) and solvents dimethylformamide (DMF, 99.8%) and n-hexane (Anhydrous, 95%) were obtained from Sigma-Aldrich. Both components of PDMS (polydimethylsiloxane, Sylgard 184), the resin dimethylsiloxane and the cure dimethyl-methyl hydrogen-siloxane were obtained from Dow Corning. The as-obtained resin was highly viscous and was hence diluted by n-hexane in a ratio of 2:1 (wt%) to facilitate electrospinning. Accordingly, the viscosity was reduced from 6380 cP to 102 cP. The measured viscosity of cure was 65 cP, so the cure material was used to form the core material as received without any further dilution.

2.2 Coaxial electrospinning

The materials and the co-electrospinning process used to prepare self-healing core-shell nanofiber mats with liquid healing agents in the core are similar to those employed in ref. ³ In brief, co-electrospinning of core-shell nanofibers^{3, 21} was conducted using the setup sketched in Fig. 1. The nanofiber shells were always formed from 8 wt% PAN solution in DMF. The fiber cores were formed either from liquid monomer of PDMS & n-hexane mixture (2:1), or its cure (dimethyl-methyl hydrogen-siloxane)-the agent which facilitates resin polymerization as PDMS. The material significance of the components used to form core-shell nanofibers in the present work stems from the fact that all three materials (PAN, resin monomer or cure) are soluble in the same solvent (DMF), which is convenient for the co-electrospinning process. Also, all of them are common inexpensive spinnable materials, which allow one to create an interwoven nanofiber matrix with either resin monomer, or cure required in vascular-like self-healing composites. The flow rates of the core and shell materials were 70 and 900 $\mu\text{L/h}$, respectively. The applied voltage was 13 kV and the needle-to-collector distance was 9 cm. All the samples were stored in

a sealed container with desiccant (at 15-19% humidity) and the experiments were conducted at room temperature (25 °C) at 40% humidity. Two coaxial nozzles of the type shown in Fig. 1 operated simultaneously depositing either PAN-resin monomer or PAN-cure nanofibers onto the same drum collector rotating at a speed of 200 rpm for 3 h, thus forming self-healing PRC (PAN-Resin-Cure) nanofiber mat.^{3, 6, 20} It should be emphasized that, as usual in electrospinning, the deposited mats had random orientations of the fibers. Since the discharge of the deposited fiber loops is relatively fast (since no build-up was observed), formation randomly mutually interwoven fibers with resin and cure in their core was thus achieved, albeit no additional characterization of this was done. Monolithic PAN nanofibers were electrospun on a similar drum collector to form PAN samples for comparison with the PRC samples. The diameters of the PAN and PRC nanofibers were 544 ± 180 nm and 578 ± 138 nm, respectively, with the difference being statistically negligible. The thicknesses of the PAN and PRC nanofiber mats were 0.089 ± 0.021 mm and 0.191 ± 0.031 mm, respectively. The fiber mat thickness was averaged after measuring the thickness at five different locations using a micrometer.³ Both PAN-Resin (PR) and PAN-Cure (PC) fiber mats were prepared and characterized in the same way. The prepared fiber samples were tested within a week, and stored in a sealed container with silica gel to prevent any possible moisture absorption or contamination before they are being tested.

As mentioned in ²², cast PAN is a partially wettable polymer with a contact angle with water (WCA) of 30-40°. On the other hand, PAN nanofiber mats are superhydrophobic due to the entrained air (the Cassie-Baxter state), with the WCA as high as 173°. ²²⁻²³ To prevent any possible contamination or a further humidity deposition the prepared fiber samples were stored in a sealed container with silica gel until they had been used.

Note also that in our previous study,²⁰ the DSC and TGA analysis of pristine PAN, PRC (PAN-Resin-Cure), PR (PAN-Resin) and PC (PAN-Cure) nanofiber mats was conducted.

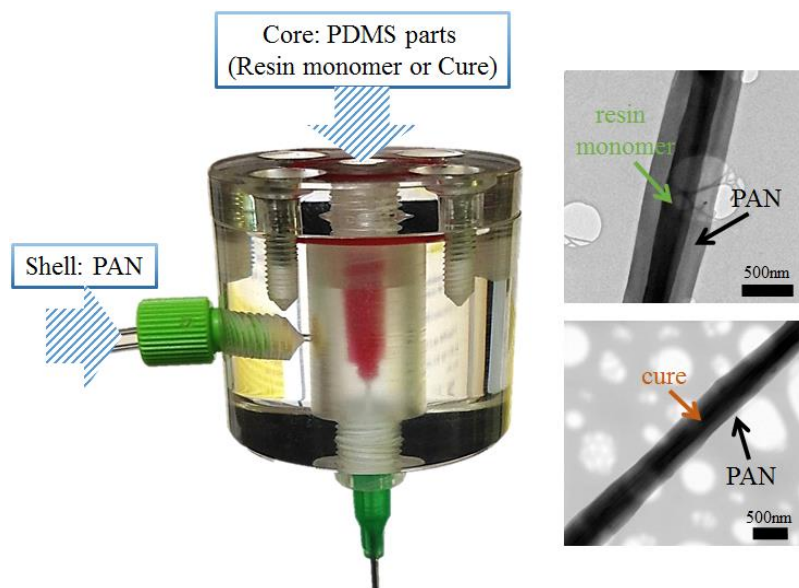


Fig. 1. One of the coaxial nozzles used to form self-healing core-shell nanofibers (on the left) and TEM images of the core-shell nanofibers with either resin monomer or cure in the core (on the right).

2.3 Tensile tests

The pristine nanofiber mat samples were employed for tensile tests using Instron 5942. The tensile tests of the nanofiber mats and the fiber-reinforced composite samples were conducted according to ASTM D7565²⁴ standard. The samples were prepared by cutting the electrospun nanofiber mats along the machine direction into rectangular strips of sizes 60×25 mm² (length $\times$ width). These rectangular samples were then fixed in the Instron 5942 machine by clamping the upper and lower ends of the samples by the pneumatic grips such that the two

clamps are separated by 20 mm. Thus the exposed sample had an initial area of $20 \times 25 \text{ mm}^2$. A 5 mm-long sharp crack was notched in the middle of the sample on the right-hand side (Fig. 2b). Then, such samples were stretched at the strain rates of 50, 10 and 1 mm/min until they completely failed due to crack propagation (mode I fracture). The load-displacement data during the tensile tests were converted into the corresponding stress-strain curves, as well as video imaging of crack propagation through the samples was conducted simultaneously. It should be emphasized that the cross-sectional area was evaluated as the product thickness $\times$ width of the sample, thus the cross-sectional porosity was not accounted for. Stretching is known to diminish the cross-sectional porosity of nanofiber mats, thus an inaccuracy this introduced diminishes as the stress and strain increase.

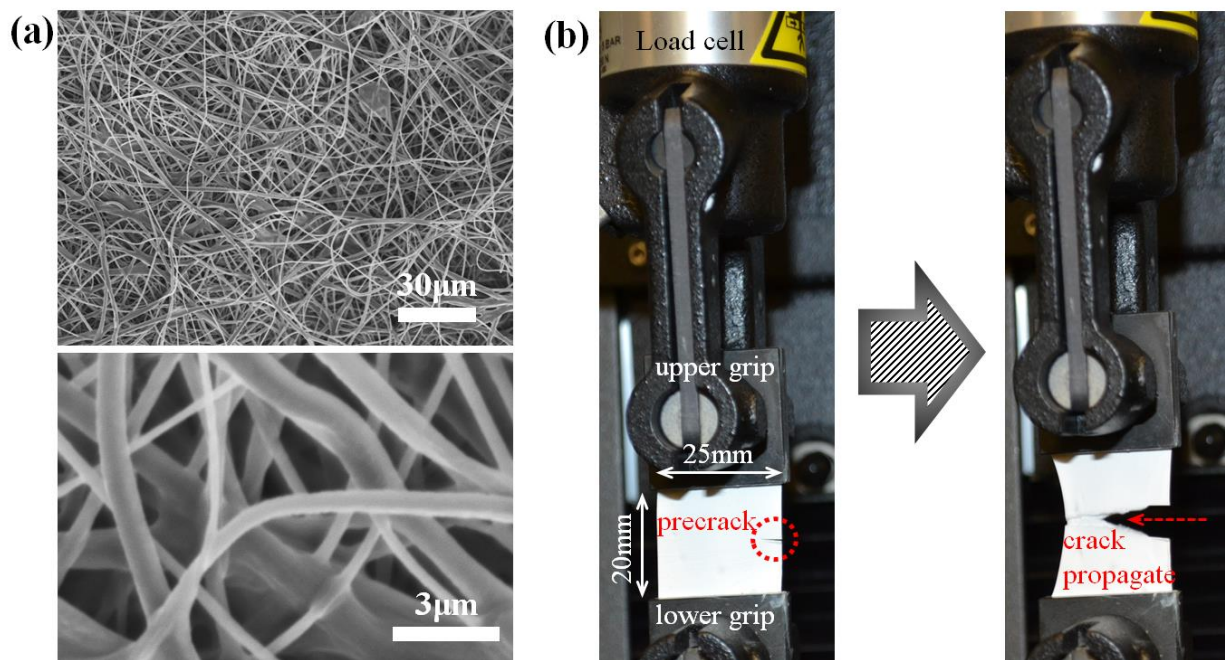


Fig. 2. (a) SEM micro-images of as-spun nanofiber mat before it had been damaged. (b) The original sample (an as-spun nanofiber mat) held between the grips of Instron 5942 and crack propagation during the tensile test.

2.4 Optical characterization

The micro-graphs and elemental analysis were obtained by SEM (Scanning Electron Microscopy)/EDX (Energy Dispersive X-ray Spectroscopy) using Hitachi S-3000 N. Transmission electron microscope (TEM) images were taken by JEM 2100F, JEOL Inc. under 200 kV operating condition.

3. Results and Discussion

3.1 Experimental observations

To observe the healing agents flowing out from the core of broken nanofibers, SEM micro-graphs had been taken for PRC nanofiber mats (Fig. 3). The fiber mat had been immersed in liquid nitrogen bath and then cut by a sharp blade. The incision made in the as-spun nanofiber mat was immediately viewed under SEM. The upper-row images in Fig. 3 had been taken 10 min after creating the crack in PRC nanofiber mats. These images revealed drops of resin or cure pending from the broken fibers after being released from the cores. The drops had been initially identified due to their shiny spherical surfaces in these images, which indicated that they were still in liquid form, similarly to the observations in ²⁵. In about 20-30 mins after creating the incision, the liquid drops were about to solidify and could be seen as matt points in the lower row images in Fig. 3. According to ²⁵, this corresponded to the resin-cure reaction resulting in the epoxy solidification. The liquid drops were found along the cut zone and their presence was a proof that healing agents had been indeed released from the core of the broken nanofibers, mixed

due to the binary diffusion process,²⁵ reacted and solidified, as at the core-to-shell mass ratio of 2.29 wt%.⁷ Currently, it is hardly possible to determine the threshold and optimal proportion of the healing agents relative to that of the matrix, albeit it seems to be sufficiently low, which had been manifested by successful self-healing revealed in the tensile, bending and adhesion tests.^{3, 6}

Note also that solidification does not happen in any core alone, since the cores contain either the resin monomer, or cure separately. Solidification happens only when they are released from broken fiber cores, mix together and the polymerization reaction proceeds. It should be emphasized that neither XRD (X-ray Diffraction), nor EDX and Raman spectroscopy can be used to analyze whether a mixed drop containing the resin monomer and cure was polymerized, and thus solidified. This can be done only by observing the change in the surface texture of a drop, as was proven in Ref. ²⁵. Such a change was also noted via a detailed inspection of the images similar to those in Fig. 3 in the present work, which proved that polymerization and solidification indeed took place in the drops in Fig. 3.

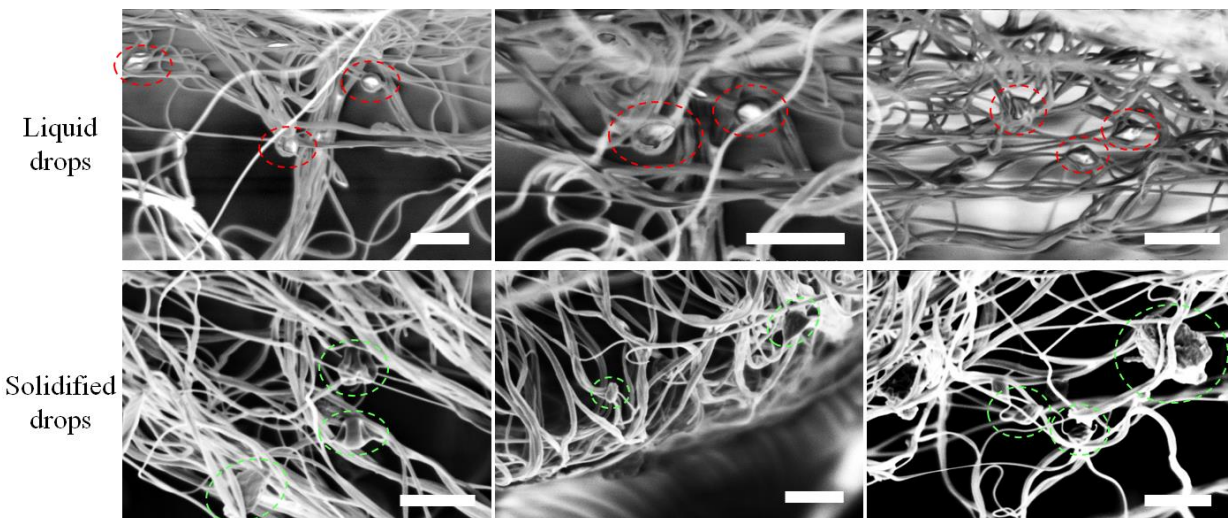


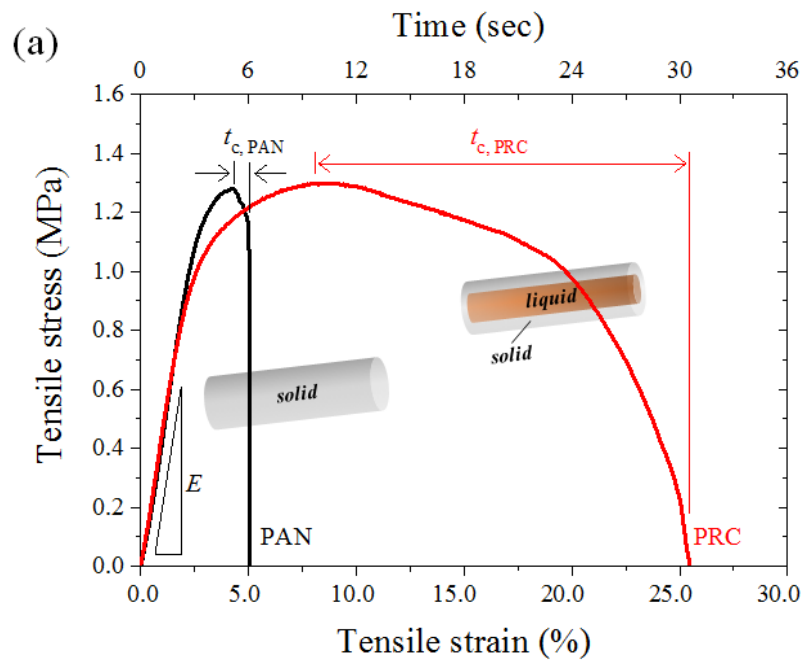
Fig. 3. SEM images of cut zone in a PRC nanofiber mat (scale bar is 5 μm). The surrounding vacuum **could have been facilitated** drop release from the fibers but such a release was also observed in open air under room pressure in our previous work.²⁰

3.2. Tensile test results

A representative stress-strain curves for PAN and PRC samples measured in tensile tests along with crack propagation in mode I are shown in Fig. 4a. The corresponding stiffness associated with the initial linear segments of the curves and the ultimate strengths achieved **were** close for the PAN and PRC nanofiber mats in the present case. Significant differences between the two curves are observed beyond the ultimate strength point. The strain-at-failure of the PRC sample **was** much larger than that of the PAN sample. The PAN sample revealed a sudden failure right after the maximum stress point, so the time interval until its complete failure ($t_{c, \text{PAN}}$) **was** short compared to that of the PRC sample ($t_{c, \text{PRC}}$). The PRC nanofiber mat **was cracking** gradually for a much longer time. The crack propagation length to the complete sample failure **was** 20 mm, i.e. the difference between the sample width 25 mm and the pre-cracked length of 5 mm **was observed**. This propagation length of 20 mm was divided by each crack propagation time (either $t_{c, \text{PAN}}$ or $t_{c, \text{PRC}}$) to evaluate the crack propagation speed, V .

Several representative images of the PAN and PRC nanofiber mat samples showing crack propagation during the tensile tests are depicted in Figs. 4b and 4c. In all the cases, the samples had been held between two grips of the Instron 5942 machine. The lower grip remained fixed during the entire experiment, while the upper grip moved upward at a constant stretching rate. Figs. 4b and 4c reveal that initially only the crack width increased^d, while the crack length

remained the same at the pre-notched value of 5 mm. Once the tensile stress had reached its maximum value, indicating that the sample had reached its ultimate strength point, the crack proceeded horizontally and its length began to increase. From the images of the sample taken at regular time intervals, the crack propagation rate was measured beyond the ultimate strength point till the crack had reached the other edge of the sample (cf. rightmost image in Figs. 4b and 4c).



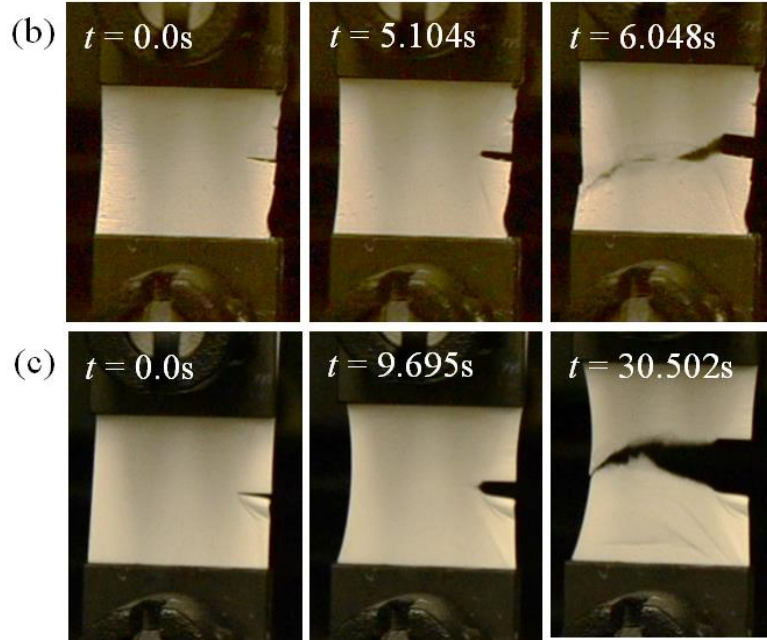


Fig. 4. (a) Stress-strain curves measured in tensile tests with pre-notched crack propagation in mode I: the black line corresponds to PAN sample, while the red line corresponds to PRC sample. The images of (b) PAN and (c) PRC samples during the tensile tests reveal crack propagation in the horizontal direction beyond the ultimate strength point. The strain rate for the tensile tests was 10 mm/min in both cases.

The tensile tests of PAN and PRC samples had been repeated at least four times (marked 1-4 in panel a and b) for each stretching rate and thus the averaged Young's moduli and crack propagation speeds were established. Figs. 5-7 summarize the results of the tensile tests conducted at strain rates of 50, 10 and 1 mm/min, respectively. The catastrophic failure of the PAN nanofiber mats had happened right beyond the maximum strength point, while that of the PRC samples was delayed to a much larger strain, which was similar to the data in Fig. 4. The crack propagation speed of the PRC samples was only about 11% of that of the PAN samples. In

other words, the PRC samples revealed a much slower crack propagation during the tensile tests, while the Young's modulus of the PAN samples was by about 22% higher than that of the PRC samples. The crack propagation was retarded by just the presence of the uncured (yet) liquid agents in the core of the core-shell PRC nanofiber mats. The presence of viscous liquids in the fiber cores introduced an additional channel of the energy dissipation. The specific value of the energy dissipation rate is of the order of $\mu(V/d)^2$, with μ being the zero-shear viscosity, V being the crack propagation velocity and d the cross-sectional fiber diameter. The viscous dissipation rate increases dramatically for sufficiently high liquid viscosities and the small fiber diameters, as was the case here. This is substantiated by the fact that, as Fig. 4a shows, the rupture of the PRC sample took about 26 s, while the rupture of the PAN sample took only 5 s in spite that all the conditions (the fiber diameter, the mat thickness and the strain rate were the same). This points at the retarding action of the liquid cores, albeit a detailed micro-mechanical theory of this phenomenon is currently unavailable.

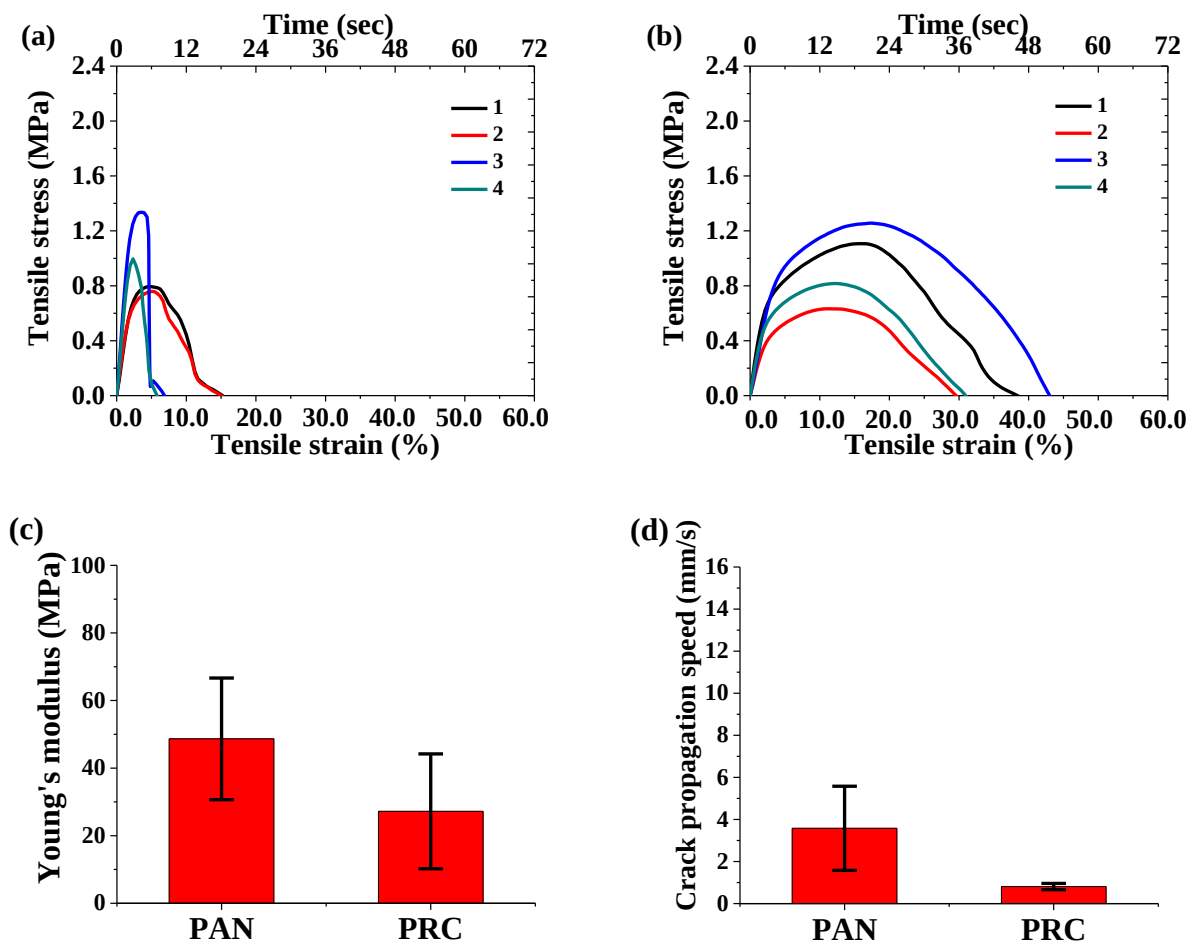


Fig. 5. Stress-strain curves of (a) PAN and (b) PRC nanofiber mat samples in tensile tests with crack propagation. The numerals in panels (a) and (b) indicate different trials. Averaged (c) Young's moduli and (d) crack propagation speeds for the PAN and PRC samples. Stretching at the rate of 50 mm/min. Here and hereinafter in Figs. 6 and 7 the numerals 1 to 4 associated with different curves denote the results from for different trials used to evaluated repeatability.

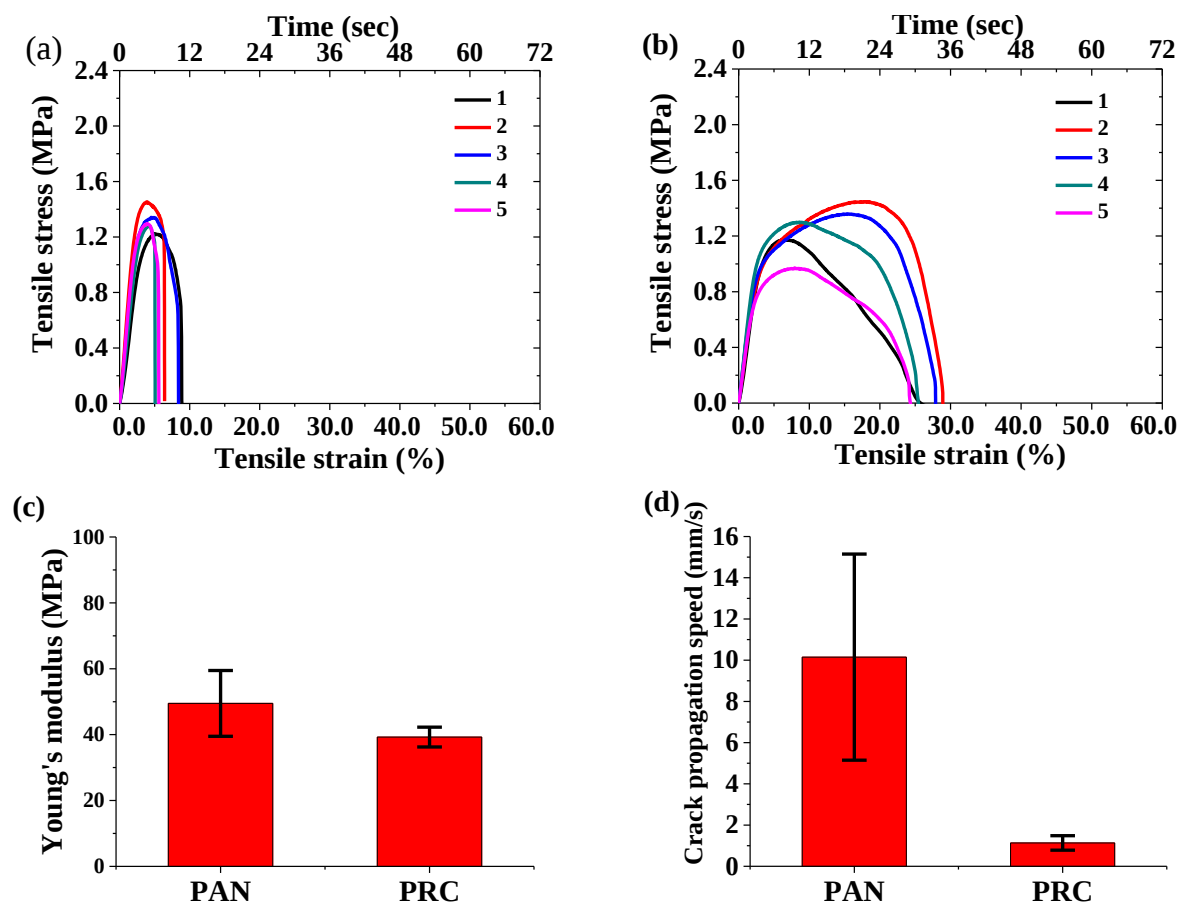


Fig. 6. Stress-strain curves of (a) PAN and (b) PRC nanofiber mat samples in tensile tests with crack propagation. The numerals in panels (a) and (b) indicate different trials. Averaged (c) Young's moduli and (d) crack propagation speeds for the PAN and PRC samples. Stretching at the rate of 10 mm/min.

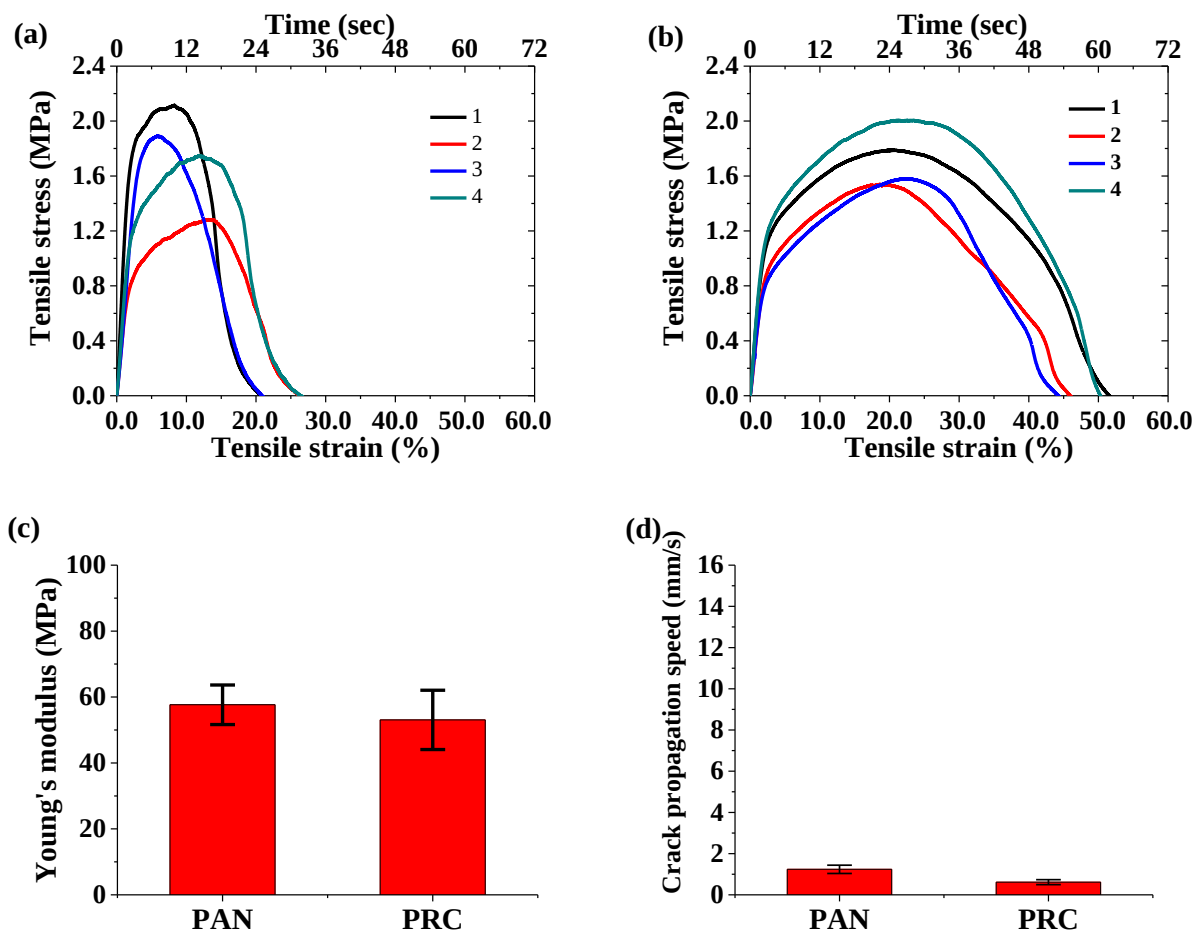


Fig. 7. Stress-strain curves of (a) PAN and (b) PRC nanofiber mat samples in tensile tests with crack propagation. The numerals in panels (a) and (b) indicate different trials. Averaged (c) Young's moduli and (d) crack propagation speeds for the PAN and PRC samples. Stretching at the rate of 1 mm/min.

The Young's modulus of the PRC samples gradually decreased^d as the strain rate increased^d from 1 to 50 mm/min (Fig. 8a). The slower^{was} the stretching, the higher^{was} the measured stiffness of the PRC samples, whereas that of the PAN samples^{was} approximately constant (cf. Fig. 8a). At^{the} lowest stretching rate of 1 mm/min, the Young's moduli of the PAN

and PRC samples were similar. Thereafter, the Young's modulus remained the same for the PAN samples, whereas it decreased for the PRC samples. The crack propagation speed of the PRC samples was approximately independent of the stretching rate and much lower than that of the PAN samples, with the latter also being strongly stretching rate-dependent (Fig. 8b). At the lowest stretching rate of 1 mm/min, the crack propagation speeds for the PRC and PAN samples were similar. Thereafter on increasing the stretching rate, the crack propagation speed for the PAN samples increased significantly, while that of PRC samples remained the same. Accordingly, the crack propagation speed at the strain rate of 10 mm/min was about 10 times lower for the PRC samples as compared to that of the PAN samples.

The strains at which the ultimate stress had been attained, denoted as the ultimate strain, for different PAN and PRC samples at different stretching rates are depicted in Fig. 8c. Since the crack propagation begins only after the ultimate stress had been attained, a higher strain at which the ultimate stress had been attained (or in other words, the higher ultimate strain) implies a longer time duration before the beginning of crack propagation. This time is denoted by t^* in Fig. 8c. As seen in this figure, PRC samples (indicated by red symbols in Fig. 8c) at all stretching rates attained the ultimate stress at higher values of strain than the corresponding PAN samples. Thus, it can be concluded that the beginning of crack propagation in PRC samples was delayed as compared to the PAN samples.

It should be emphasized that t^* is the time interval from the beginning of the tensile tests till the ultimate stress point had been reached, whereas t_c is the time interval from the ultimate stress point till a complete sample rupture. Thus, t^* indicates an initial delay in crack propagation, while t_c is indicative of the crack propagation speed in a sample. Fig. 8 indicates that both t^* and

t_c are longer for the PRC samples. Hence, it can be concluded that the cracks began to grow later and grow slower in the PRC samples as compared to their counterpart PAN samples.

As for the comparison of the PR and PC mats, their behavior was found to be quite similar to each other. It should be emphasized that their Young's moduli and the ultimate stress and strain were slightly different from those of the PRC mats. In Fig. 8a, the Young's moduli of the PR and PC mats are higher than that of the PRC mat, and even higher than that of the PAN mat at some points. The ultimate stress and strain of the PR and PC samples was higher and lower, respectively, than that of the PRC sample (see Fig. 8c). However, still the crack propagation speed in the PR and PC samples was similar to that in the PRC sample, while being lower than that in the PAN sample for all the three strain rates.

It should be emphasized that irrespective of the data scatter involved and manifested by the error bars, Fig. 8c reveals a clear delineation of the data for the PRC mats from the data for PAN, PR and PC mats. The resin polymerization by the curing agents associated with microscopic damage prior to crack propagation was present only in the PRC mats of all the above-mentioned mats, and thus had been responsible for the recorded delay in the sample failure.

In general, the higher the applied load, the shorter time period (t^*) is required to achieve the beginning of the rupture.²⁶ The longer time to failure of the PRC samples as compared to that of the PAN samples allows one to speculate that the stress relaxation (memory effects) could take place in the PRC samples. The stress relaxation in the PRC nanofibers is presumably associated with the presence of a liquid core in these nanofibers. Indeed, in addition to the elastic parameter of the material, Young's modulus E , associated with the solid polymeric shell of the fibers, appears another parameter, the zero-shear viscosity μ , associated with the liquid core.

Accordingly, the characteristic stress relaxation time $\theta=\mu/E$ arises, which determines stress relaxation in time t , typically in the form of the exponential fading memory $\exp(-t/\theta)$ [23]. An additional factor is that liquid in the nanofiber core can act as a plasticizer. Plasticizers are often added during manufacturing processes to improve the mechanical properties of polymers. Polymer chains are getting easier to rotate and move with larger free volume between the chains.²⁷ Plasticizers help to decrease Young's modulus and increase stretchability and resistance to cracking.²⁸⁻³⁰ In summary, the presence of liquid curing agents in the fiber cores in the PRC mats could provide an additional energy dissipation channel, making them viscoelastic and stretchable, as well as curing microscopic damage by means of the resin polymerization prior and during crack propagation.

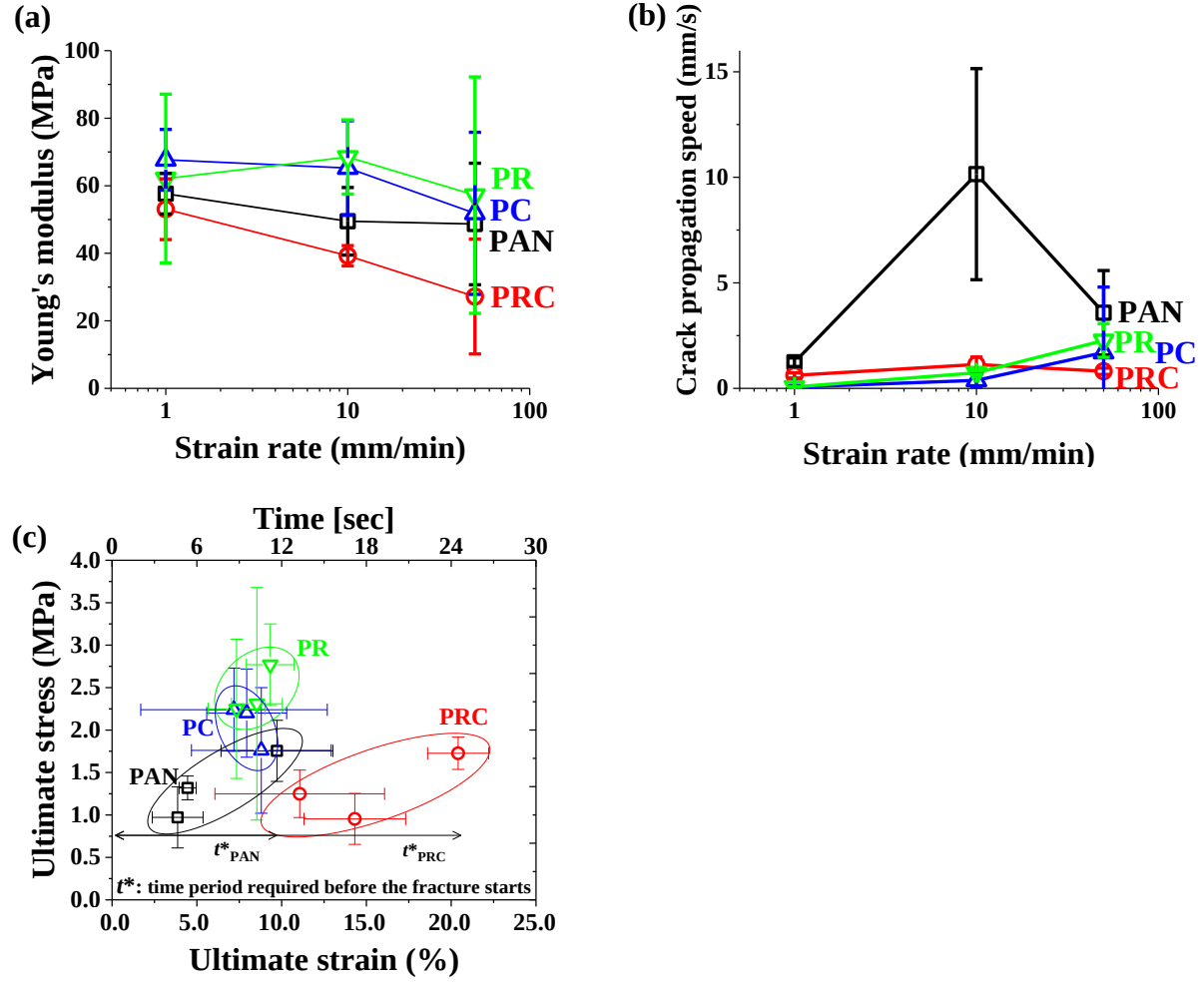


Fig. 8. Material parameters of the PAN, PRC, PC and PR samples. (a) Young's moduli. (b) Crack propagation speeds. (c) Ultimate stress versus ultimate strain.

4. Experimentally measured crack shapes versus theory

The as-spun PRC and PAN nanofiber mats revealed irregular crack shapes and intermittent crack propagation as in Fig. 4. Also, to study crack shapes and crack propagation rates, composite samples were formed with the electrospun PRC and PAN nanofibers embedded in them. The PAN/PRC nanofiber mat was cut in a pieces of $25 \times 60 \text{ mm}^2$ and then encased in

PDMS (10:1 wt. ratio) matrix. The thickness of such PRC- and PAN-containing composites was in 0.61 ± 0.16 mm and 0.52 ± 0.26 mm, respectively. Similarly to tensile tests of PRC and PAN nanofiber mats, a 5 mm-long sharp crack was pre-notched in the middle of the sample on the right-hand side of these composites. Then, crack propagation under tension was observed. Similar observations with pure PDMS samples (without embedded nanofibers) were done, however, the sample stiffness in this case did not allow to achieve a uniform crack propagation, as can be seen in Fig. 9a.

Figs 9b and 9c show the shapes of the cracks as they propagate across the PDMS-PRC and PDMS-PAN composite samples, respectively. The theoretically predicted shape under the assumption of the Kelvin-Voigt viscoelasticity is sketched in Fig. 10, as it follows from the results of ³¹. Such shapes can resemble to some extent the experimental images in Figs. 9b-i for various crack lengths and pre-notch positions. The PDMS-PRC and PDMS-PAN samples which had a pre-notch at the right end are shown in panels 9b, 9g-i and 9c-f, respectively. The initial incision had different lengths of 5, 2 and 10 mm in these cases. The initial incision was also located in the middle of the samples in panels 9f and 9i for PDMS-PAN and PDMS-PRC samples, respectively. Overall, the PDMS-PAN and PDMS-PRC samples revealed similar trends in crack propagation, smoothness and uniformity in the crack boundaries and propagation rate. Especially, in Fig. 9d, the experimentally observed evolution of the crack shape at the final stages match quite well with the theoretical predictions.

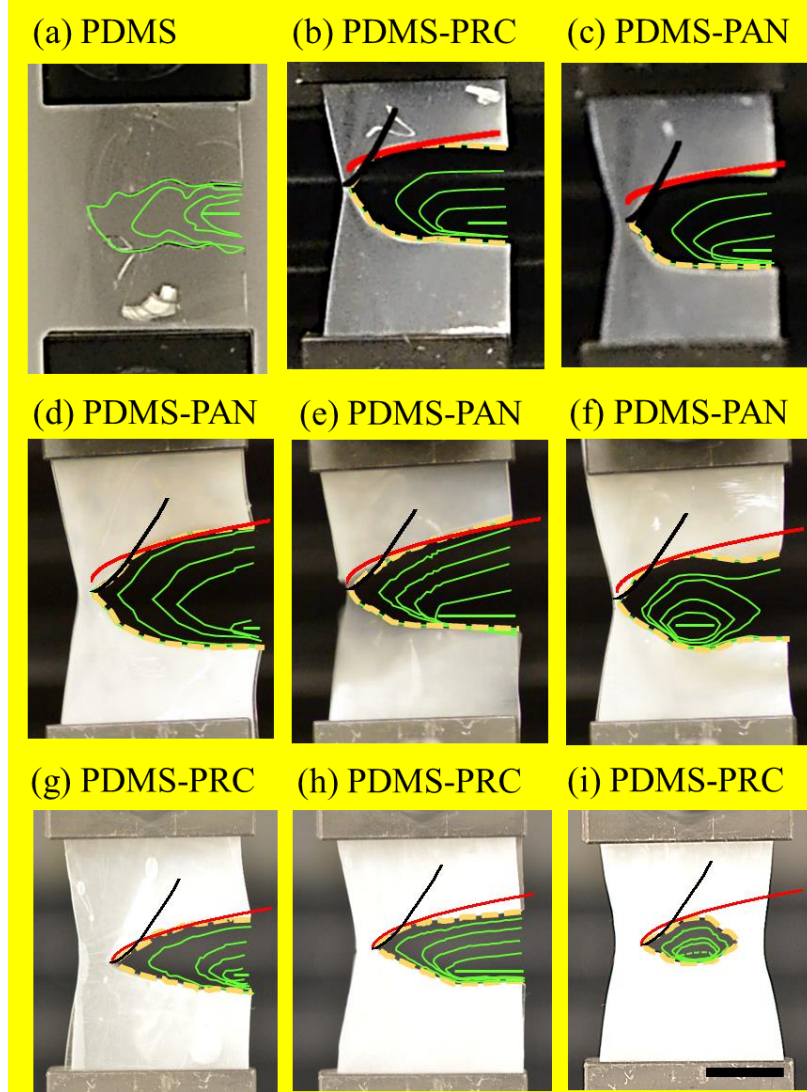


Fig. 9. Crack evolution in (a) pure PDMS, (b, g-i) PDMS-PRC, and (c)-(f) PDMS-PAN composite samples. The pre-notched incision (shown by green solid horizontal bars) lengths: (a)-(c) $l_0 = 5$ mm, (d, g) $l_0 = 2$ mm, (e, h) $l_0 = 10$ mm, (f, i) $l_0 = 5$ mm. The initial incision was located on right edge for panels (a-e, g-h), and at center for panel (f, i). Four different colors are used to demarcate curves with different physical meaning, namely, black color is used for the near-field asymptotic, red color – for the far-field asymptotic, green color – for the intermediate contours of the propagating cracks, and the dashed yellow lines correspond to the final crack shapes. The theoretical predictions shown by black and red solid lines correspond to the asymptotics

$[x-l(t)]^{3/2}$ and $[x-l(t)]^{1/2}$, respectively. The theoretical predictions are compared with the last snapshots in all the panels, since for these snapshots the best resolution of the crack tip is available. Scale bar is 10 mm.

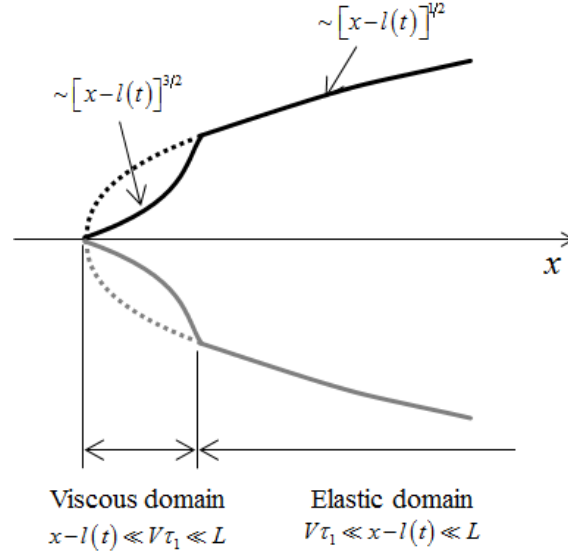


Fig. 10. Crack shape predicted for Kelvin-Voigt viscoelastic material.

5. Experimentally measured crack propagation versus theory

An increase in crack length l due to an external load p is stable when³²

$$\frac{dp}{dl} > 0 \quad (1)$$

For a crack pre-notched at the center of a plate of width $2h$, the stress intensity factor K_I is given as³²

$$K_I = p \sqrt{\pi l \sec \frac{\pi l}{2h}} \quad (2)$$

The fracture toughness, K_{IC} , is a material property and for our composites can be calculated using Eq. (2) for the stress values corresponding to the ultimate strength measured in section 3. The yield stress, σ_s can be obtained by fitting the stress-strain curve of the composites to the phenomenological equation for uniaxial stretching³³⁻³⁵

$$\sigma_{xx} = \sigma_s \tanh\left(\frac{E}{\sigma_s} \varepsilon\right) \quad (3)$$

where E is Young's modulus, σ_s is the yield stress, σ_{xx} is the tensile stress and ε is the tensile strain.

Rendering Eqs. (1) and (2) dimensionless and introducing dimensionless variables l^* , p^* and λ

$$l^* = \frac{l}{h}, \quad p^* = p \frac{\sqrt{\pi h}}{K_c}, \quad \lambda = \frac{\pi K_c^2}{12h\sigma_s^2} \quad (4)$$

the region of instability on the l^* , p^* plane is found as³²

$$\cos \frac{\pi l^*}{2} < l^* p^{*2} \left[1 + \lambda p^{*2} \left(1 + \frac{\pi l^*}{2} \sec \frac{\pi l^*}{2} \right) \sec \frac{\pi l^*}{2} \right] \quad (5)$$

Equation (5) corresponds to curve II (blue) in Fig. 11, where the domains below and above this curve correspond to stable and unstable crack propagation, respectively.

The crack growth in the stable domain from an initial dimensionless crack length of $2l_0^*$ is given by ³²

$$l^* - l_0^* = -\lambda \left[l^* p^{*2} \sec \frac{\pi l^*}{2} + \ln \left(1 - l^* p^{*2} \sec \frac{\pi l^*}{2} \right) \right] \quad (6)$$

Equation (6) corresponds to the solid line curve I (red) in Fig. 11. A crack in any body begins to behave as an ideally brittle crack when the dimensional term $\Delta l^* > 2$ where ⁽³²⁾

$$\Delta l^* = \frac{12}{\pi} \frac{\sigma_s^2 (l - l_0)}{K_c^2} \quad (7)$$

Equation (7) corresponds to curve III (green) in Fig. 11.

For comparison with the above-mentioned theoretical results, PAN composite samples were prepared similarly to section 4. Rectangular strips of PAN nanofiber mats were encased in PDMS (10:1) matrix. The width of the samples ($2h$) was 25 mm. An initial incision of length 2 mm was made at the sample center (cf. Fig. 9f). Its initial crack length was $2l_0$. The composite PAN samples were then stretched at a uniform stretching rate of 8 mm/min using Instron 5942, while taking snapshots of the developing crack at regular time intervals. The dimensionless load p^* was obtained from the stress-strain data, while the dimensionless crack length l^* was measured from the snapshots.

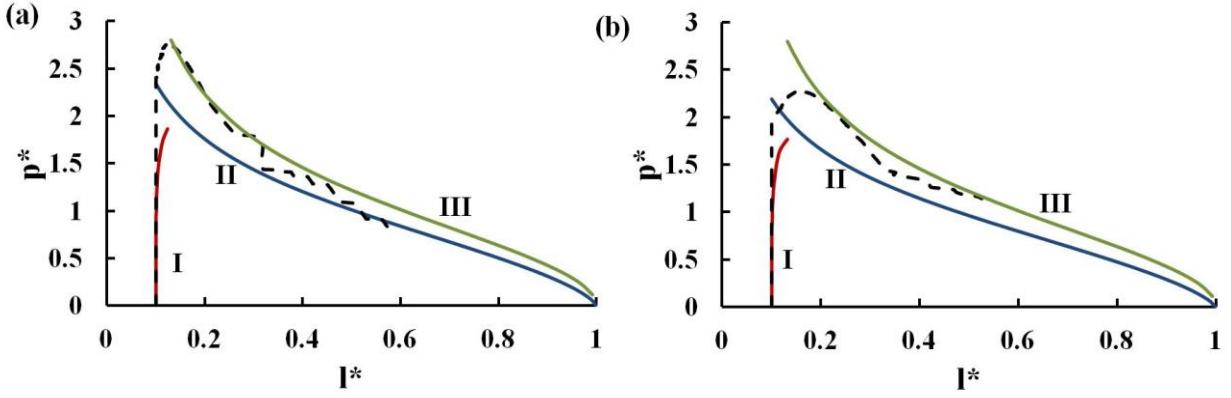


Fig. 11. Comparison of the experimental results on crack propagation with the theory. Panels (a) and (b) correspond to two different trials. Red lines I correspond to Eq. (6), blue lines II correspond to Eq. (5), green lines III correspond to Eq. (7) and black dotted lines correspond to the experimental data.

Fig. 11 depicts the results of two experimental trials (shown by black dotted lines) and compares them with the theoretical lines I (red) and II (blue). Note that since the parameters K_c and λ are calculated using the maximum stress and yield stress values, the theoretical curves for each experimental set vary from one another. Two such experimental trials are shown in Fig. 11. Initially, the crack growth is stable, as seen from the overlapping curves of the experimental data with curves I. As the dimensionless load p^* keeps on increasing, the crack length l^* crosses from the stable to unstable domain (crosses curve II). The crack length then begins to increase in an unstable wiggly way close to the ideal brittle crack trend. That continues beyond the ultimate stress point of the composite, and leads to a complete sample rupture.

The PDMS-PAN samples do not contain any healing agent and hence the crack length l is a direct function of the external load p . As seen in Figs. 4-8, crack propagation in PRC samples

is delayed significantly and failure of these samples occurs at a much larger strain, which was attributed to the presence of liquid cores and the associate viscoelastic stress relaxation. The current theory considers continuous crack propagation under an external load p . It does not account for the effect of the liquid cores. Furthermore, the fracture toughness K_c of the sample will change once the liquid cores would be accounted for. The current theory is based on the calculation of K_c at the ultimate strength and assumes the composite material to be the same throughout the crack propagation distance. Currently, there is no method of calculating or measuring K_c for the PDMS-PRC samples. Hence, the existing theory could not be compared to the observed crack propagation for the PDMS-PRC samples.

5. Conclusions

The electrospun core-shell nanofibers contained liquid resin and cure inside the cores were formed and studied in tensile tests with a pre-notched crack propagation. These measurements were accompanied by the optical crack observations until a complete sample failure, as well as by SEM observations of release and cure of the healing materials from the cores of the damaged nanofibers. Crack propagation speeds were measured. It was found that the crack propagation speed in the self-healing PRC nanofiber mats is lower than that in the non-self-healing PAN nanofiber mats down to about 10%. Composite materials were also formed by encasing the self-healing PRC nanofibers, as well as the non-self-healing PAN nanofibers, in PDMS matrix. Crack propagation was more stable in such composites and the shapes of the propagating cracks partially resembled those predicted for Kelvin-Voigt viscoelastic materials. Crack propagation was also analyzed from the stability point of view. It was shown that in

nanofiber-containing composites crack propagation is initially stable, then becomes unstable and resembles that of the ideal brittle crack until a complete sample failure.

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